I. THE REACTIVITY OF PHENANTHRENE-9, 10-DICARBOXYLIC ACID ANHYDRIDE

II. THE STRUCTURE OF MONOCROTALINE

III. ADDENDUM

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FRANCIS JAMES SPRULES

B.A., University of Toronto, 1936

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I. THE REACTIVITY OF PHENANTHRENE-9,10-DICARBOXYLIC ACID ANHYDRIDE

A perusal of the literature concerning phthalic anhydride and its derivatives indicates that all but one of the reactions characteristic of these substances occurs by the addition of the second reactant across the anhydride group. Therefore, the effect of substituents in the 3- and 6-positions on the rate of reaction of these derivatives relative to that of phthalic anhydride itself is not as large as would be expected, if the reactions proceeded by the addition of the second reactant to one of the carbonyl groups. This is due to the fact that the anhydride group is more distant from the substituents than the carbonyl groups are.

Phenanthrene-9,10-dicarboxylic anhydride may be regarded as dibenzophthalic anhydride. Jeanes and Adams[1] have reported that this compound reacts with aromatic hydrocarbons in the presence of aluminum chloride and with *o*-phenylene diamine in the expected manner. Weizmann, Bergmann and Berlin[2] have also reported that the reaction of this substance with phenyl magnesium bromide proceeds in the normal manner. The reactivity and chemical properties of phenanthrene-9,10-dicarboxylic acid anhydride were investigated more completely during the present investigation.

By the reaction between phenanthrene-9,10-dicarboxylic acid anhydride,[3] a 46 per cent yield of 9-aceto-10-phenanthroic acid was isolated. The expected condensation product underwent decarboxylation during the reaction and rearrangement by hydrolysis when the reaction mixture was decomposed. Reactions of this type proceed by addition to the carbonyl group.[4] The fact that this much product was isolated, indicates that these *ortho* substituents do not hinder the reaction appreciably. The keto-acid was identified by conversion to the ethyl ester.

The remaining reactions which are characteristic of phthalic anhydride proceed by the addition of the second reactant to the anhydride group. Therefore good yields would be predicted. When phenanthrene-9,10-dicarboxylic acid anhydride was allowed to react with methyl magnesium iodide, a 60 per cent yield of 9-aceto-10-phenanthroic acid was isolated. The acid was converted to the ethyl ester.

An 84 per cent yield of dibenzofluorescein was prepared from phenanthrene-9,10-dicarboxylic acid anhydride and resorcinol.[5] A yellow lactoidal and a red quinoidal isomer were isolated in the

ratio of 5 to 2. Both substances were amorphous solids and solutions of either in ethanol exhibited characteristic green fluorescence. The yellow isomer was converted to a colorless crystalline diacetate and to the dimethyl ether by means of diazomethane. A rust-colored and a yellow isomer of the dimethyl ether were isolated.

The yellow isomer of dibenzofluorescein was converted to dibenzoeosin.[6] A light pink and a red isomer were isolated. They were both amorphous solids. The light pink isomer was converted to a colorless crystalline diacetate and to a dimethyl ether. An almost colorless and a bright red isomer were isolated in the latter case.

When phenanthrene-9,10-dicarboxylic acid anhydride was allowed to react with phenol in the presence of zinc chloride,[7] two products were obtained. These are believed to be phenol dibenzophthalein and dibenzofluoran. The yield of the former was 6 per cent and the latter 42 per cent. The phthalein exhibited color reactions in acid and alkaline solution which were similar to those of phenolphthalein. Both products were yellow amorphous solids. Phenanthrene-9,10-dicarboxylic acid anhydride was converted to 9,10-dicarbethoxy-phenanthrene by means of ethyl sulfate and alkali. An attempt was made to condense this ester with ethyl acetate in order to prepare dibenzodiketohydrindene.

Phenanthrene-9,10-dicarboxylic acid anhydride reacted readily with a mixture of nitric and fuming nitric acids. A mixture of nitro compounds was obtained.

Phenanthrene-9,10-dicarboxylic acid anhydride possesses many of the chemical properties of phthalic anhydride. However, it is somewhat less reactive.

II. THE STRUCTURE OF MONOCROTALINE

Monocrotaline was isolated from the seeds of *Crotalaria spectabilis* Roth by a method which differed from the one previously reported [8] and which led to the isolation of higher yields of the material. This substance has been found to be an alkaloid which is similar to the Senecio, Trichodesma, and Heliotropium alkaloids.[9]

One of the methods commonly used to degrade these alkaloids is alkaline hydrolysis. Monocrotaline was cleaved in this manner. The products were retronecine, an acid which has be called monocrotic acid, and carbon dioxide. The purpose of this problem was to determine the constitution of monocrotic acid.

Monocrotic acid was optically inactive and possessed the empirical formula $C_7H_{12}O_3$. It was readily converted to the methyl ester. The expected ester was formed from 3,5-dinitrobenzoyl chloride and this acid. Monocrotic acid possessed a hydroxyl and carboxyl group. Unless a cyclic structure was involved, there must be an olefin group. The methyl ester absorbed one mole of hydrogen in the presence of Raney nickel at 120° and 2000 lbs. This indicated the presence of an olefin group which is difficult to hydrogenate.

Monocrotic acid reacted with 2,4-dinitrophenylhydrazine also. These facts were reconciled by postulating the existence of a carbonyl group that readily enolized. Then it was found that monocrotic acid could be cleaved by sodium hypobromite. In addition to bromoform approximately equal amounts of *dl*- and *meso*-dimethyl succinic acid were isolated. [10] The *meso*-form was identified by conversion to the neutral *p*-bromphenacyl ester and the corresponding succinanilic acid.[11] These compounds gave no depression of the melting point with authentic samples prepared from synthetic *meso*-dimethyl succinic acid.[12] In this way, monocrotic acid was identified as α,β-dimethyl levulinic acid.

In contrast to the above evidence for the existence of both *dl*-forms of monocrotic acid, no evidence for the existence of stereoisomers was found when the 2,4-dinitrophenylhydrazone was fractionally crystallized. The best method of explaining these observations was by synthesis. The method used should be one that would lead to the formation of one of the *dl*-forms of α,β-dimethyl levulinic acid exclusively. By means of some reaction that did not involve the asymmetric carbon atoms, it should be possible to synthesize each of the *dl*-forms of α,β-dimethyl levulinic acid from meso- and *dl*-dimethyl succinic acid or one of their derivatives.

In order to find a method that would be suitable for this purpose, several attempts to synthesize levulinic acid from succinic acid derivatives were made. These were as follows: The reaction between the half ester half acid chloride and cadmium methyl[13]; the reaction between succinic anhydride and methyl magnesium iodide,[14] cadmium methyl or dimethyl aluminum chloride; the reaction between succinimide and methyl magnesium iodide, and the reaction between succinic anhydride and malonic ester. A 35 per cent yield of the desired product was obtained in

the first case only. However, when this method was used with the half ester half acid chloride of *dl*-dimethyl succinic acid, none of the desired product was isolated.

III. ADDENDUM

THE REACTION BETWEEN ACTIVATED VINYL BROMIDES AND COMPOUNDS WHICH CONTAIN REACTIVE METHYLENES

Hurtley [15] has reported that compounds which possess a reactive methylene group, may be condensed with *o*-brombenzoic acid in the presence of copper bronze or copper acetate. The reaction between *o*-brombenzoic acid and malonic ester, diethyl ethyl malonate, diethyl phenyl malonate and phenyl acetic ester resulted in the formation of unsatisfactory yields of the desired product. When *o*-brombenzoic acid was condensed with dibenzoylmethane in the presence of copper bronze, a good yield of 2′-carboxydesoxybenzoin was obtained. When copper acetate was used in place of copper bronze, the amount of pure material was much smaller. This agrees with the observations of Hurtley.

It was interesting to see if this type of reaction could be carried out in the aliphatic series. Bromfumaric acid was allowed to react with resorcinol, dibenzoylmethane and malonic ester. The product isolated from the last reaction was a liquid which possessed a reactive halogen. The desired condensation did not occur but the reactants underwent a Michael condensation.

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VITA

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